Paper #90

Optimization of Test Parameters for Time-Temperature Superposition Testing and Effect of Heat History on Time-Temperature Superposition Results

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Abstract

The Time-Temperature Superposition (TTS) principle is helpful for determining high or low frequency properties beyond the capability of the dynamic mechanical test instrument. While there has been a handful of research conducted on this test method from its discovery to the present, there has not been any research into how many frequencies or what temperature step size should be included to obtain the best results while minimizing instrument time. In this study, recommendations will be made for these test parameters. The effect of heat history on TTS results will also be discussed.

Introduction

The Time-Temperature Superposition (TTS) principle relates long test times for various viscoelastic properties at a desired operating temperature to short test times for the same properties at a higher temperature and it relates very short test times at the desired operating temperature to longer test times at colder temperatures. For viscoelastic properties, the test time is best reflected in the frequency setting for the test. For example, if the available test instrument is capable of only 500 Hz and characterization at 10 kHz is needed, those properties can be obtained utilizing this principle and testing at colder temperatures.

The relationship between temperature and test time was first published in the 1950s. Three of the main researchers were Malcolm Williams, Robert Landel, and John Ferry. These three looked at a variety of polymers (both high molecular weight[1] and low molecular weight[2]), along with other glasses or glass forming liquids[2]. They also established the idea of using a shift factor called a_T, which they define as “a single temperature-dependent parameter which represents the ratio of any relaxation time at temperature T to its value at an arbitrary reference temperature T_0”[1]. Because of their research, this analysis technique has been labeled as WLF.

Since the original WLF publication, other researchers have conducted research on the TTS principle. Each has focused on various aspects or applications of the principle. From a literature search on the keywords “time-temperature superposition parameters,” two research studies appeared to be on the topic of interest. However, upon in depth review, their topics were actually 1. Generalizing the WLF fit equation[3] and 2. Verifying the values for coefficients C1 and C2 of the WLF equation given in the 1955 paper[4]. Both of these papers focus on the parameters of the WLF equation itself and not on the test parameters of a TTS test, i.e. how many frequencies and what temperature step to use. Because of this finding, this research study was undertaken and it will give recommendations on how many frequencies and what temperature step should be used in a TTS test to maximize overlap in the analysis while minimizing instrument time.

Experimental

Compound and Mixing Procedure

In this study, most of the work was performed on a model filled solution styrene butadiene rubber (S-SBR) compound. The formula is given in Table 1. One portion of the work, the effect of heat history and softening, was performed on a HNBR compound mixed previously. The

HNBR compound was available for testing while the S-SBR compound was being mixed and molded. Additionally, it had the most surface area available for test specimens compared to any of the other compounds that are being considered for evaluation in a follow-up study. During the course of the main study (detailed below), the same analysis was performed on the S-SBR compound as had been performed on the HNBR compound to determine the effect of heat history and softening on it since HNBR is a more robust polymer, i.e. more resistant to temperature effects.

Material	Model Filled SBR
First Pass	
S-SBR (Buna VSL 4525-0)	100.00
Carbon Black (N324)	15.00
Silica (Ultrasil 7000 GR)	65.00
Silane (SCA985)	5.20
Stearic Acid	1.50
Oil (Vivatec 500)	24.00
Masterbatch 1	**210.70**
Second Pass	
Zinc Oxide	1.90
Okerin Wax 7240	2.00
6PPD	2.00
Wingstay 100	0.50
Masterbatch 2	**217.10**
Third Pass	
Sulfur	1.05
CBS	0.91
DPG	1.05
Total phr	**220.11**

Table 1: Chemical Composition of Model Filled SBR Compound

The compound was mixed on a Farrel BR laboratory size mixer. The rotor speed was increased during stages 1 and 2 at the 3.5’ and 1.5’ marks, respectively, in order to reach the desired hold and drop temperature. The third stage drop temperature was reached after about 2.5 minutes. The mixed rubber was milled for one minute on a two roll mill after completion of each stage.

Stage	**Rotor speed (rpm)**	**Temperature (°C)**	**Ram Pressure (psi)**	**Hold time (min)**	**Hold and Drop Temperature (°C)**
1	65	65	50	2	160
2	65	65	50	0	150
3	60	50	50	0	110

Table 2: Mixer and mixing conditions during the three stages of compound mixing.

Test Procedures

Before starting on the TTS tests, a strain sweep was conducted on a Metravib +150 Dynamic Mechanical Thermal Analyzer (DMTA) on all of the materials to potentially evaluate in a follow-up study. From these results, a dynamic strain level within the linear region for all of the compounds was chosen to be used for the rest of the testing (Figure 1).

The TTS testing was also conducted on a Metravib +150 DMTA. Fourteen different frequency steps and ten different temperature steps were investigated in two stages. A fresh test specimen was used in each test.

In the first stage, the frequency setting was evaluated by stepping through fourteen different step sizes. The chosen frequency range was 1 to 100Hz and these step sizes ranged from 100 linear steps, i.e. every 1Hz, to 2 logarithmic steps, i.e. 1, 10, and 100Hz. The temperature range was 25°C to 41°C spaced in 4°C increments. The dynamic strain was 0.1% and the static displacement to dynamic displacement ratio was 1.3.

In the second stage, the temperature setting was evaluated by stepping through ten different step sizes. The chosen temperature range was 25°C to 65°C and these step sizes ranged from 1°C steps to 10°C steps. The frequency range was 1 to 100Hz with the number of logarithmic steps determined from the first stage. The dynamic strain was 0.1% and the static displacement to dynamic displacement ratio was 1.3. Based on previous experience with TTS tests, it was decided to not exceed the 10°C step size in order to ensure there would be at least one point of overlap when constructing the master curves. While this may seem like a preconceived bias, if there are no overlapping data points between temperature steps, then a meaningful master curve cannot be constructed.

The last stage of the testing was to run a full TTS experiment with the findings from the first two stages of the research. This meant that the frequency range was 1 to 100Hz with the number of logarithmic steps determined from the first stage. The temperature range was expanded to -50°C to 100°C, but used the temperature step size determined from the second stage. The dynamic strain was 0.1% and the static displacement to dynamic displacement ratio was 1.3.

Initial peer discussions brought about the question, are all of the tests necessary or could one long TTS test be conducted and then pared back in the analysis to generate the other conditions? This lead to the question: What effect does heat history and softening play on TTS results?

To evaluate this question, three sets of test conditions were chosen. In the first test, 24 logarithmic steps were used for the frequency and 1°C steps were used from 25°C to 55°C. The dynamic strain was 0.1% and the static displacement to dynamic displacement ratio was 1.3. In the second test, six logarithmic steps were used for the frequency and 1°C steps were used from 25°C to 55°C. The dynamic strain was 0.1% and the static displacement to dynamic displacement ratio was 1.3. In the third test, six logarithmic steps were used for the frequency and 5°C steps were used from 25°C to 55°C. The dynamic strain was 0.1% and the static displacement to dynamic displacement ratio was 1.3. In the data analysis, the results from the first test were pared back to mimic the results from the second test and the results from the second test were pared back to mimic the results from the third test. Additionally, the results from the first test were further pared back to mimic the results from the third test.

Results and Discussion

Effect of Heat History and Softening

Because the S-SBR compound was being mixed when this question needed initial evaluation (i.e. ahead of conducting the main testing), specimens of HNBR were used. This compound was chosen because it had more surface area available to take test specimens from compared to the other compounds that will be potentially evaluated in a follow-up study. However, because HNBR is a more robust compound, meaning it is more resistant to temperature effects, the analysis was repeated on the S-SBR compound during the course of the main testing as the step sizes used in these three tests were used in the main testing as well. Both sets of results are presented here.

The results from the three tests were put into Excel and the master curves were generated. The raw data from the first test was pared back to look like the raw data from the second test. A separate table was generated where the data set from the second test was divided by the data set of the first test creating a ratio. These ratios of the results were then analyzed; the closer these ratios were to unity, the more identical the data sets were to each other. An average ratio for each property was calculated. The highest and lowest average ratios were then found to determine the spread in the data and if there was any significant difference in the two sets of results based on a 95% confidence, i.e. +/- 5%. The same was repeated for the second test to the third test and then for the first test to the third test.

From the testing on the HNBR compound, for the comparison of the first data set to the second, the highest average ratio was 1.0292 and the lowest ratio was 0.9594. For the comparison of the second data set to the third, the highest average ratio was 1.0345 and the lowest ratio was 0.9496. For the comparison of the first data set to the third, the highest ratio was 1.0061 and the lowest ratio was 0.9487. These ratios were plugged into the percent difference equation using unity as the known value (i.e. ((ratio-unity)/unity) x 100). Using the confidence limit of +/- 5% and knowing that the largest absolute percent difference was 5.12%, it can be concluded that there is essentially no significant difference between the three data sets, which means that there is no significant effect of heat history or softening on the HNBR compound.

From the testing on the S-SBR compound, for the comparison of the first data set to the second, the highest average ratio was 1.100 and the lowest ratio was 0.8617. For the comparison of the second data set to the third, the highest average ratio was 1.019 and the lowest ratio was 0.9722. For the comparison of the first data set to the third, the highest ratio was 1.122 and the lowest ratio was 0.8616. These ratios were also plugged into the percent difference equation using unity as the known value. Using the confidence limit of +/- 5% and knowing that the largest absolute percent difference from unity was 13.84%, it can be concluded that there is a significant difference between the three data sets, which means that there is a significant effect of heat history or softening on the S-SBR compound.

TTS Testing – Step Size Evaluations

Fourteen different frequency step sizes were investigated over a frequency range of 1 to 100Hz. These varied from 2 log steps (or 3 data points) up to 100 linear steps (or 101 data points). The results for each test were plotted and horizontally shifted into master curves using 25°C as the reference temperature. The results for 18 log steps were then chosen as the "standard" results. This step size was chosen as the "standard" because it had one of the lowest root mean square error values out of all of the frequency steps tested. Additionally, there were five test conditions with longer overall test times, which allowed for checking on the heat history or softening effect again by comparing their results with the results from the 18 log steps (Figures 10 – 14). The results for the tests with fewer frequency steps were compared to the results from the 18 log steps to determine the range of frequency step sizes that allow for shorter test time while not decreasing the accuracy of the final result (Figures 2 – 9). From this comparison, it was determined that the absolute minimum frequency step size was 6 log steps (or 7 data points) (Figure 3). The results for 2 log steps and 4 log steps were noticeably sparse when compared to the results for 18 log steps. The largest frequency step size that still allows for shorter test time was determined to be 12 log steps (or 13 data points) (Figure 7). A frequency step size of 14 log steps (or 15 data points) can be used if there is sufficient time allowed for the testing (Figure 8). Any test conducted with a frequency step size larger than this does not improve the quality of the shift and only adds extra data points.

Ten different temperature step sizes were investigated next. The temperature range tested was 25°C to 65°C. The steps ranged from every 1°C to every 10°C with testing conducted at each step size in between. For the temperature step sizes at or below 5°C, the specimen was given 2 minutes to equilibrate to the new temperature. For the temperature step sizes above 5°C, the specimen was given 3 minutes to equilibrate to the new temperature. The results for each test were plotted and horizontally shifted into master curves using 25°C as the reference temperature. The results for the 3°C step size were then chosen as the "standard" results. This temperature step was selected because it had one of the lowest root mean square error values out of all of the temperature steps tested. Additionally, it allowed for comparing to the smallest step sizes, namely 1°C and 2°C, while still having many more data points compared to the larger step sizes. By comparing the 3°C results to both the 1°C and 2°C results, the heat history or softening effect could be evaluated again (Figures 15 – 16). The results for the larger temperature steps were compared to the 3°C step results to determine the range of temperature step sizes that allow for shorter test time while not decreasing the accuracy of the final result (Figure 17 – 23). From this comparison, it was determined that the smallest temperature step that would yield a shorter test was 4°C (Figure 17). If there is sufficient time for the test, then a step size of 3°C can be used. The largest temperature step size allowed was determined to be 7°C (Figure 20). If a temperature step size greater than 5°C is to be used for a test at or above room temperature, it is recommended to extend the equilibration time by one minute (to 3 minutes). For temperatures that are below room temperature, it is recommended to use an equilibration time of 5 minutes. If the coldest temperature of a TTS test is to be the first temperature evaluated and if it is sufficiently below room temperature, then it is recommended to use an equilibration time of 20 to 30 minutes.

Conclusion

The results from the testing yielded three main conclusions. First, it was seen that, for a model filled S-SBR compound, the heat history or softening of the material had a significant effect on the results. This meant that, in this study, twenty-four different tests had to be conducted rather than being able to conduct two or three long tests and then cut the data back to the other conditions of interest. Second, it was determined that the frequency step size should be between 8 log steps and 12 log steps with an absolute minimum of 6 log steps. This allows for shorter test times while not reducing the quality of the shifted results. Third, it was determined that the temperature step size should be between 4°C and 7°C. Again, this allows for shorter test times while not reducing the quality of the shifted results. If there is a sufficient turnaround time on a project, then a temperature step size of 3°C can be used. The necessary equilibration time at each temperature depends on a few factors, but generally ranges between 2 minutes and 5 minutes whether above or below room temperature, respectively.

Future Work

There are two main ideas that the authors would like to pursue in the future. One is to test a TTS experiment on six different filled compounds and one unfilled compound using the conditions determined in this paper. Additionally, these seven compounds will be tested on a Metravib VHF104 instrument from 1kHz to 10kHz using the determined frequency step size. Then the results from the high frequency instrument will be compared with the master curve results to determine the accuracy of the shifted results. The second idea comes from this comparison and that is to evaluate if horizontal shifting alone provides a sufficient comparison to the high frequency results or if vertical shifting is necessary to achieve the best overlap with the high frequency results.

References

1. M. L. Williams, *J. Phys. Chem.*, **59**, 95 (1955)
2. M. L. Williams, R. F. Landel, J. D. Ferry, *J. Am. Chem. Soc.,* **77**, 3701 (1955)
3. L. Dagdug, L. S. Garcia-Colin, *Physica A*, **250**, 133 (1998)
4. B. Wang, G. Chang, X. Lin, W. Guo, *4th International Conf. on Mechanical Materials and Manufacturing Engineering*, 2016

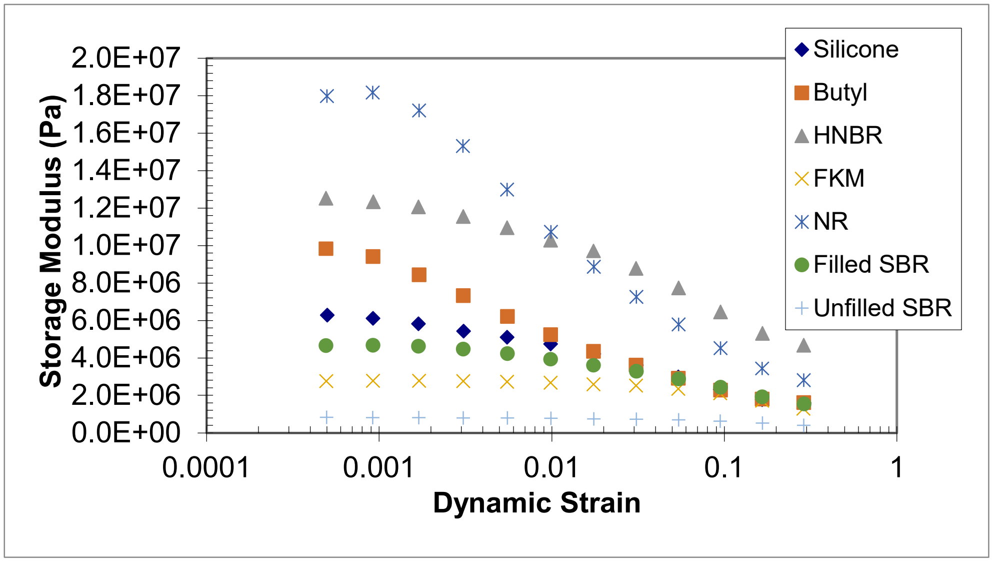

Figure 1: Strain Sweep Results (from second sweep)

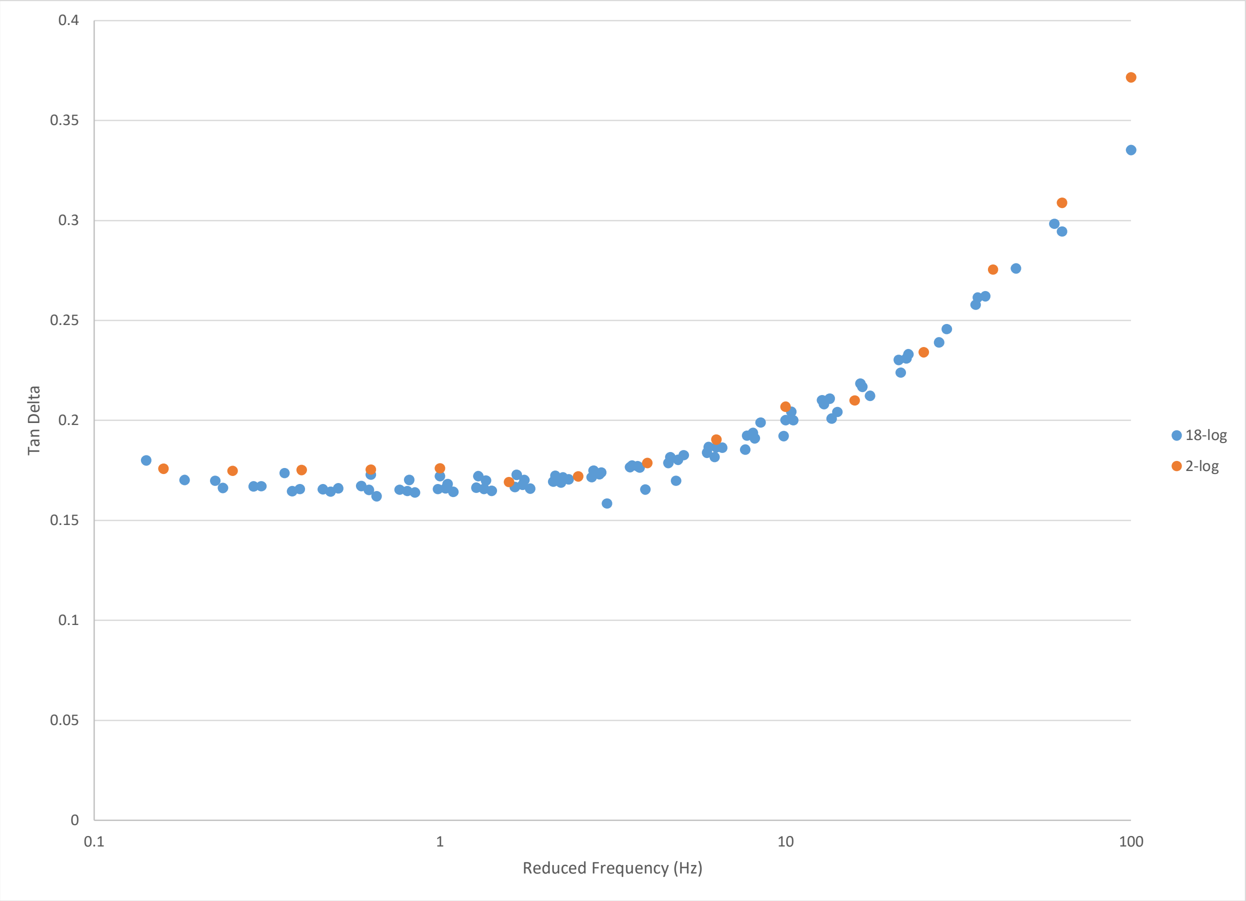

Figure 2: Frequency Evaluation: 2 log steps vs. 18 log steps (orange vs. blue)

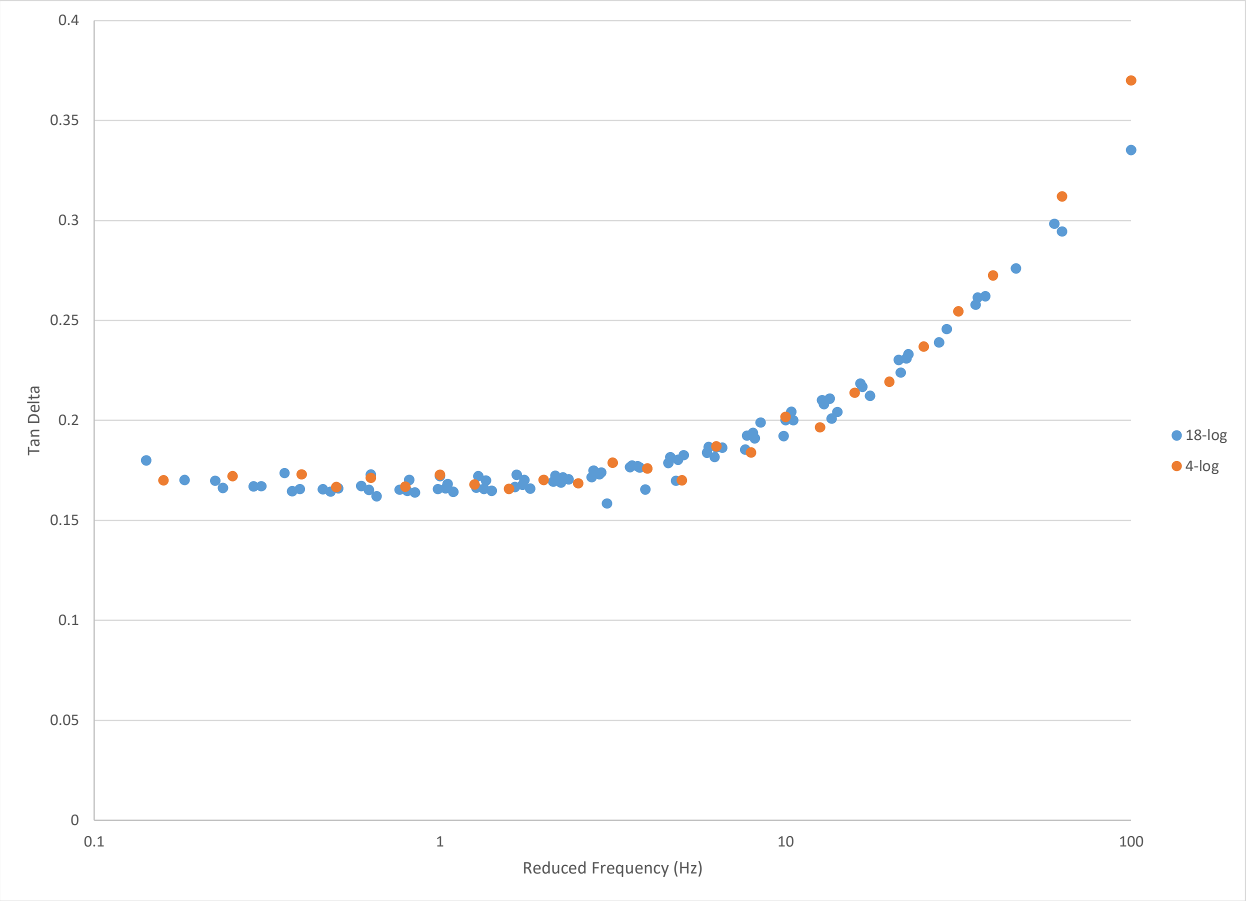

Figure 3: Frequency Evaluation: 4 log steps vs. 18 log steps (orange vs. blue)

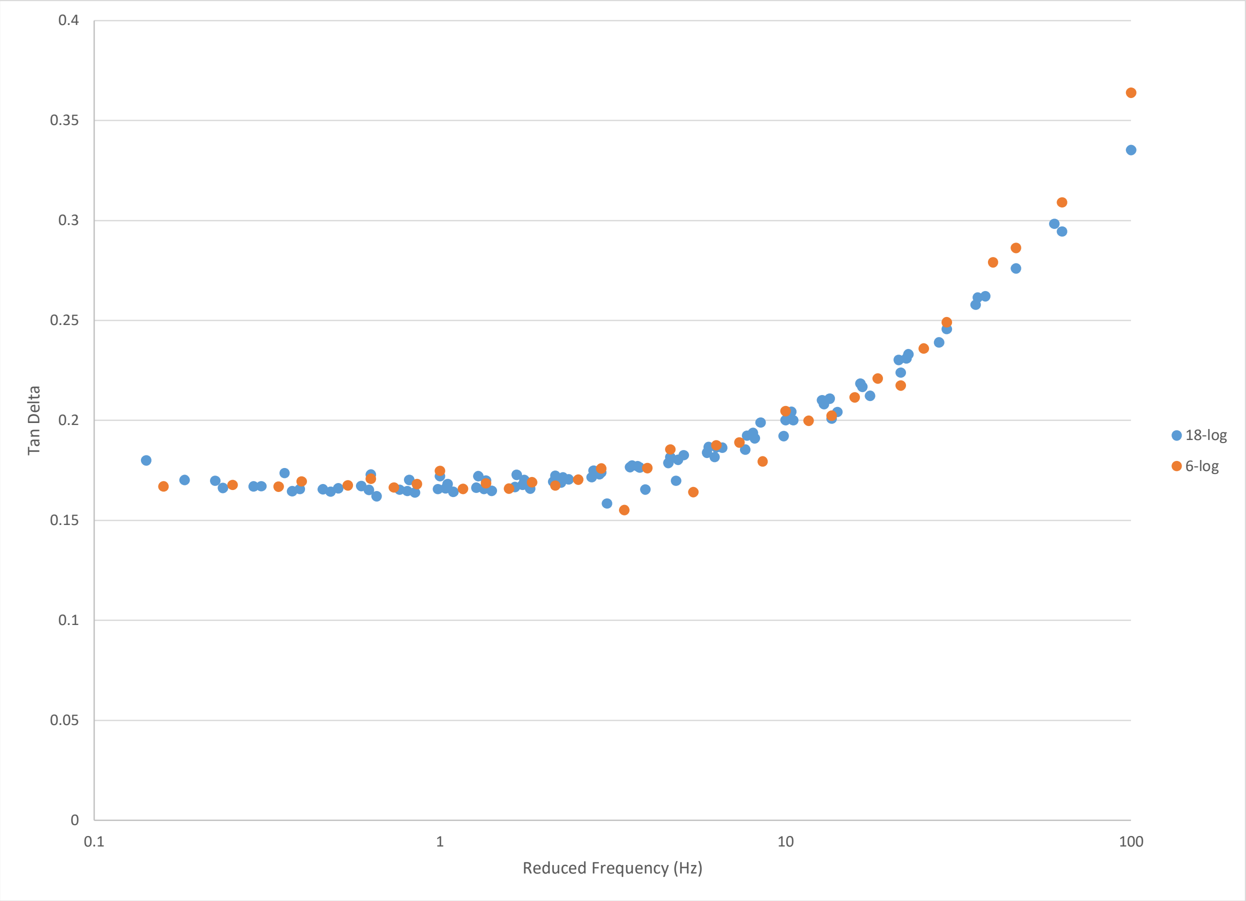

Figure 4: Frequency Evaluation: 6 log steps vs. 18 log steps (orange vs. blue)

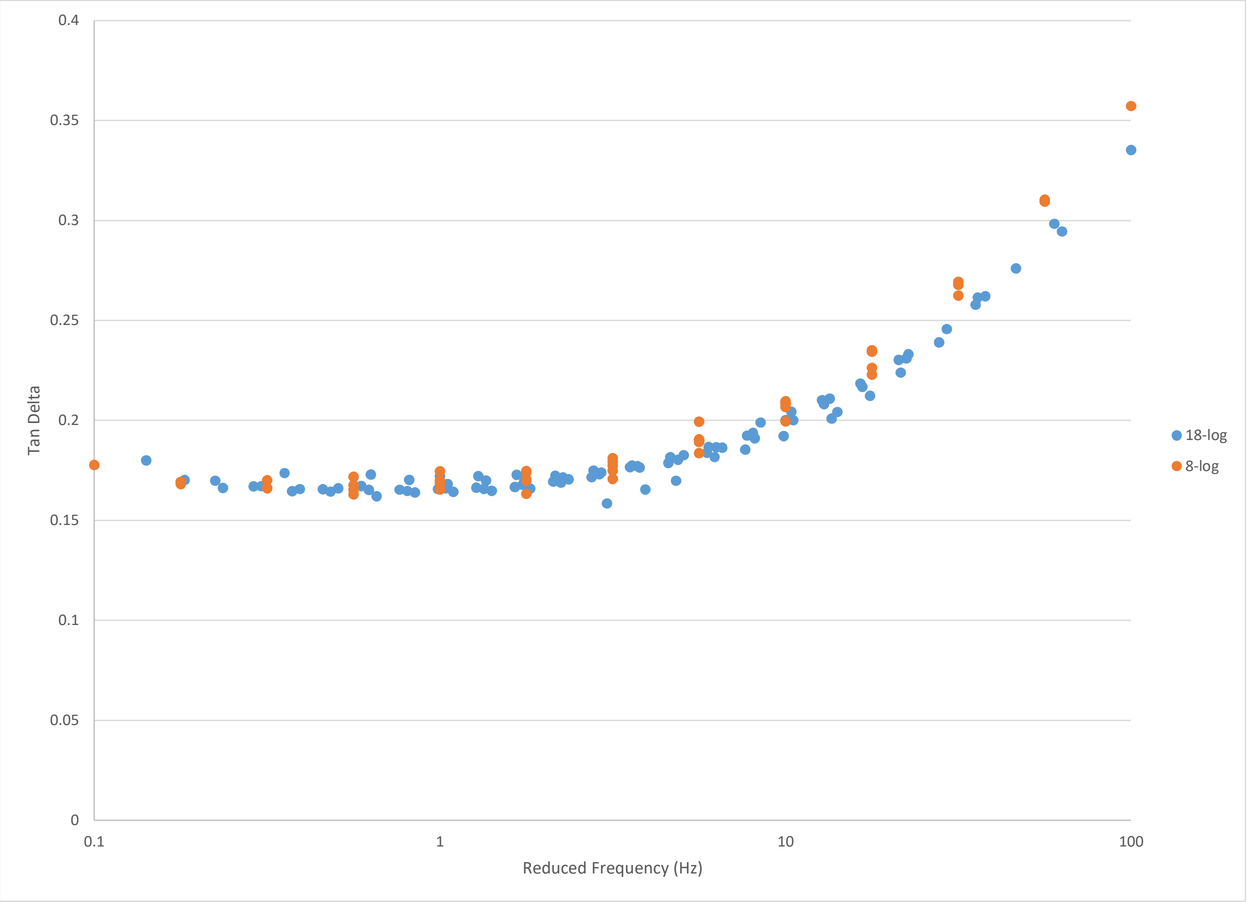

Figure 5: Frequency Evaluation: 8 log steps vs. 18 log steps (orange vs. blue)

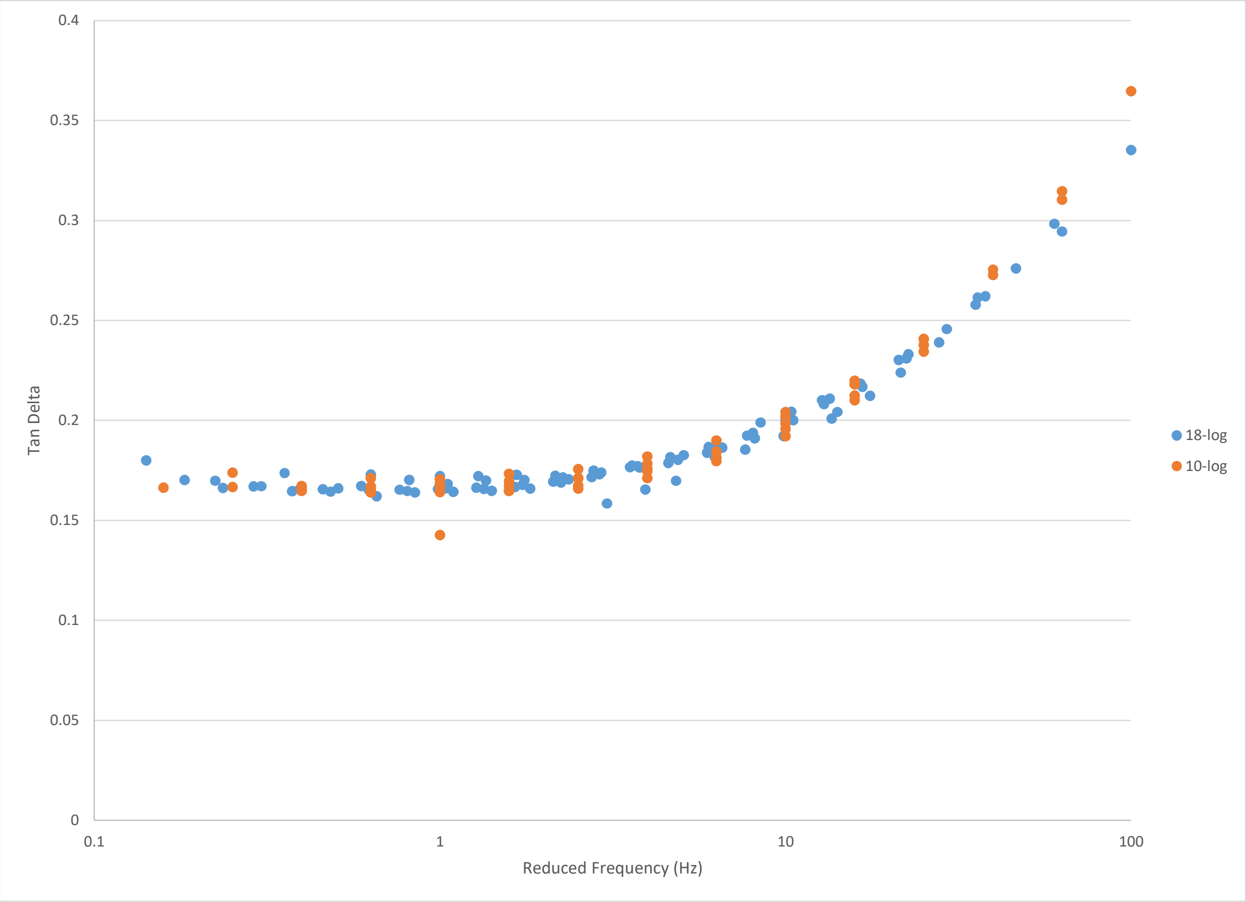

Figure 6: Frequency Evaluation: 10 log steps vs. 18 log steps (orange vs. blue)

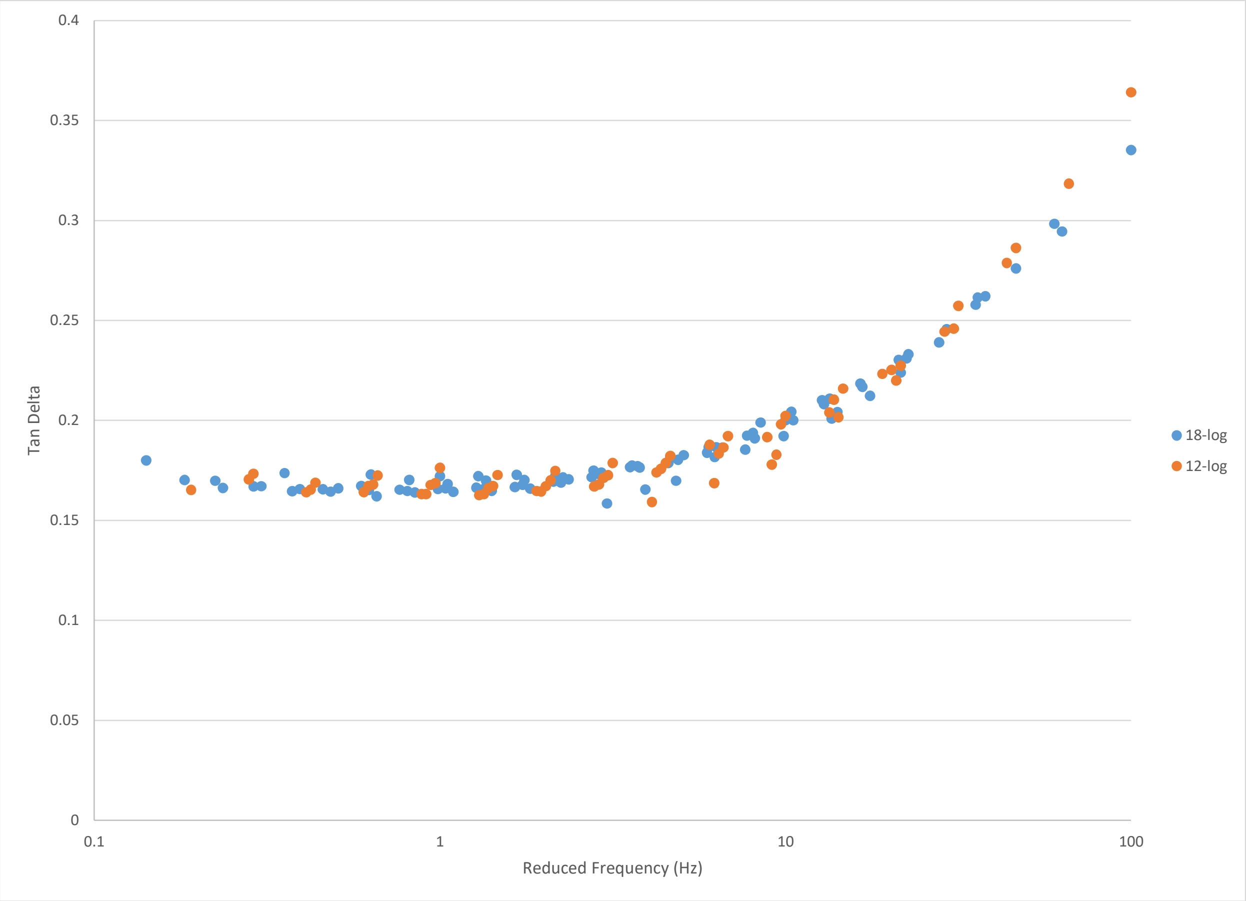

Figure 7: Frequency Evaluation: 12 log steps vs. 18 log steps (orange vs. blue)

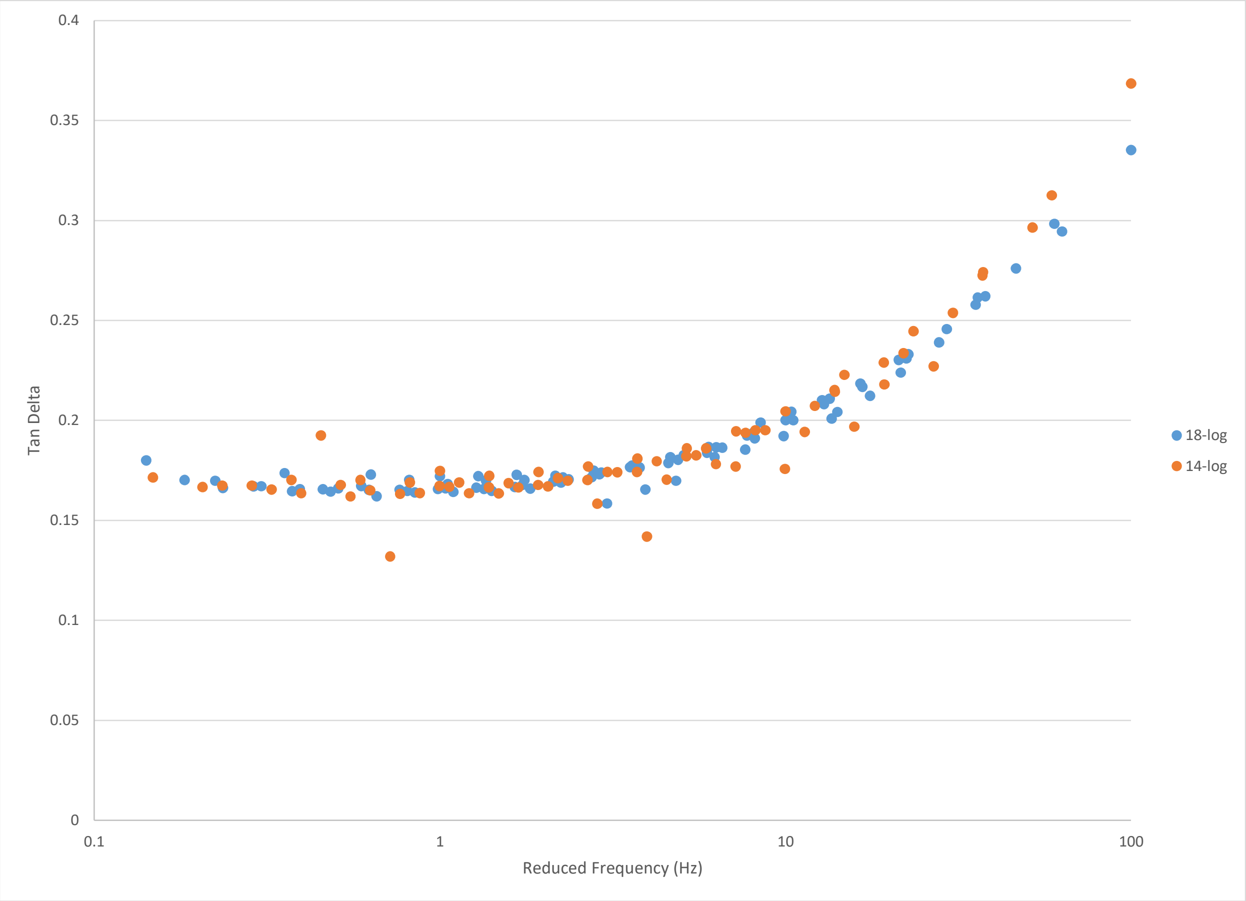

Figure 8: Frequency Evaluation: 14 log steps vs. 18 log steps (orange vs. blue)

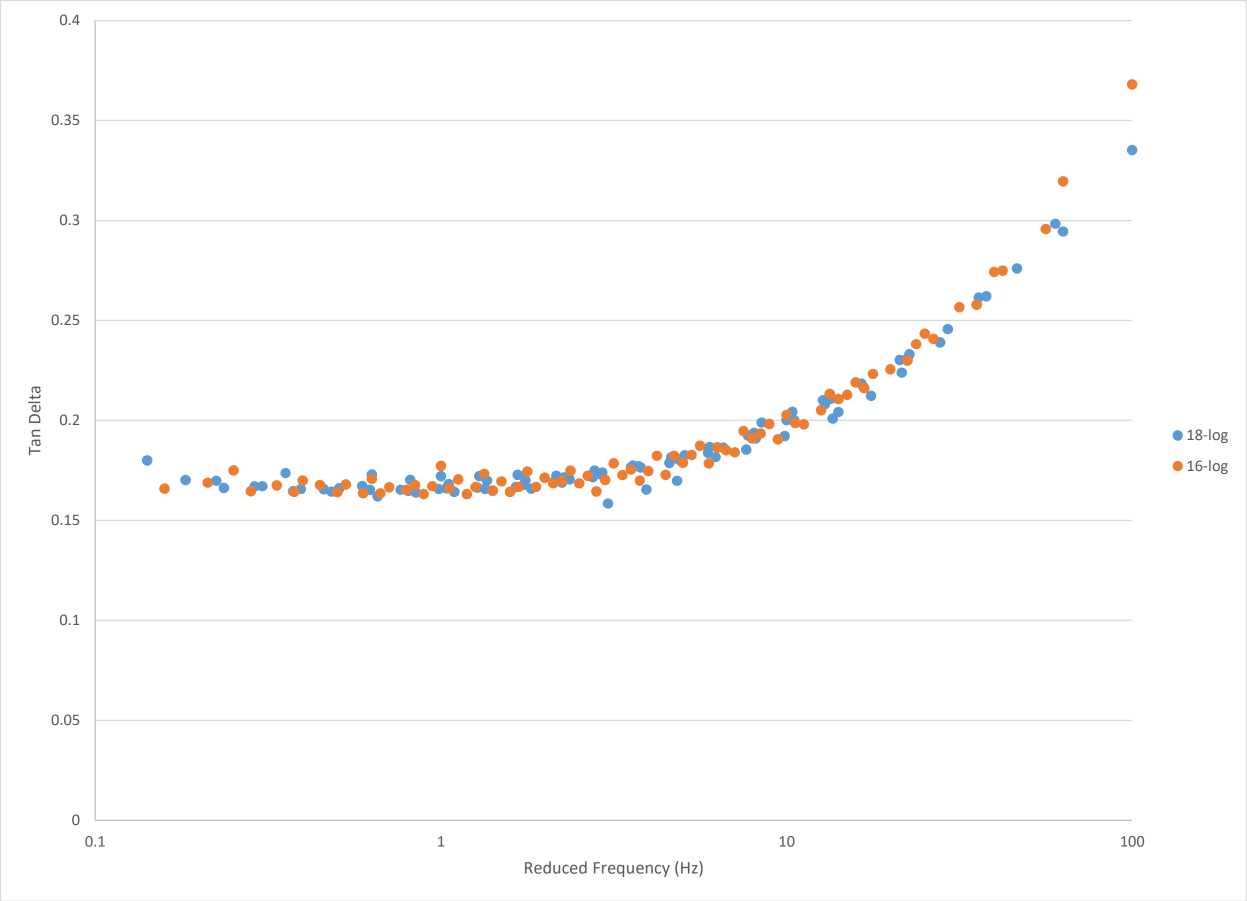

Figure 9: Frequency Evaluation: 16 log steps vs. 18 log steps (orange vs. blue)

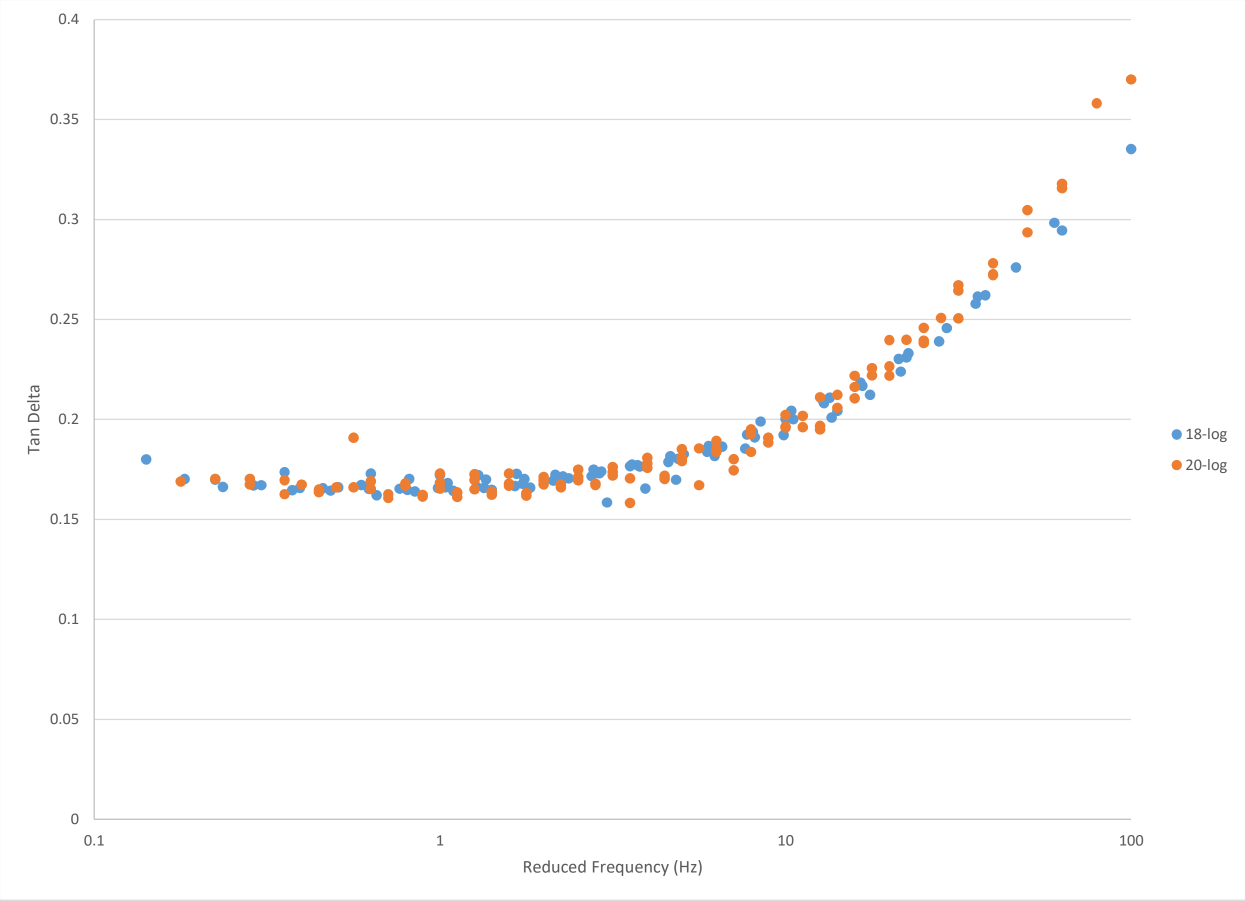

Figure 10: Frequency Evaluation: 20 log steps vs. 18 log steps (orange vs. blue)

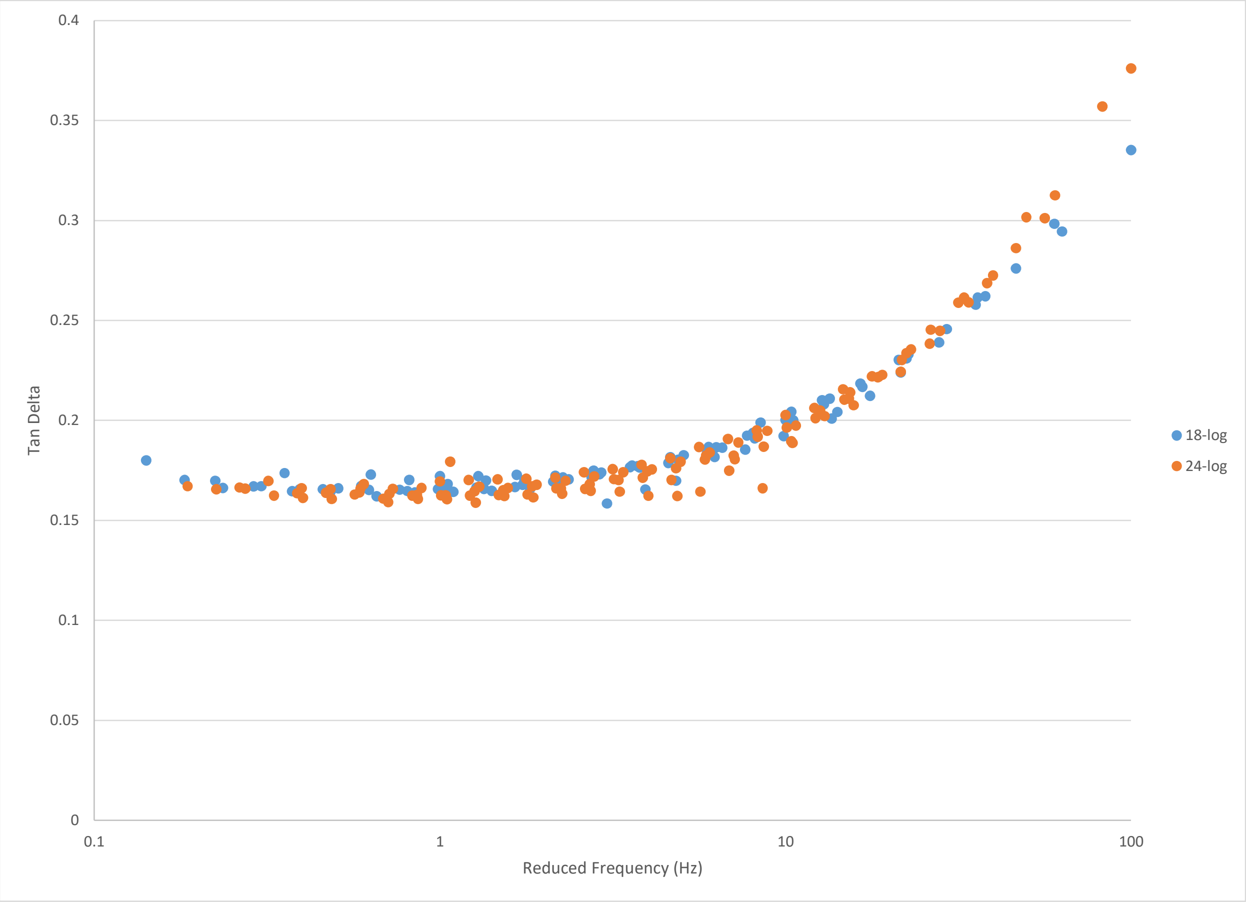

Figure 11: Frequency Evaluation: 24 log steps vs. 18 log steps (orange vs. blue)

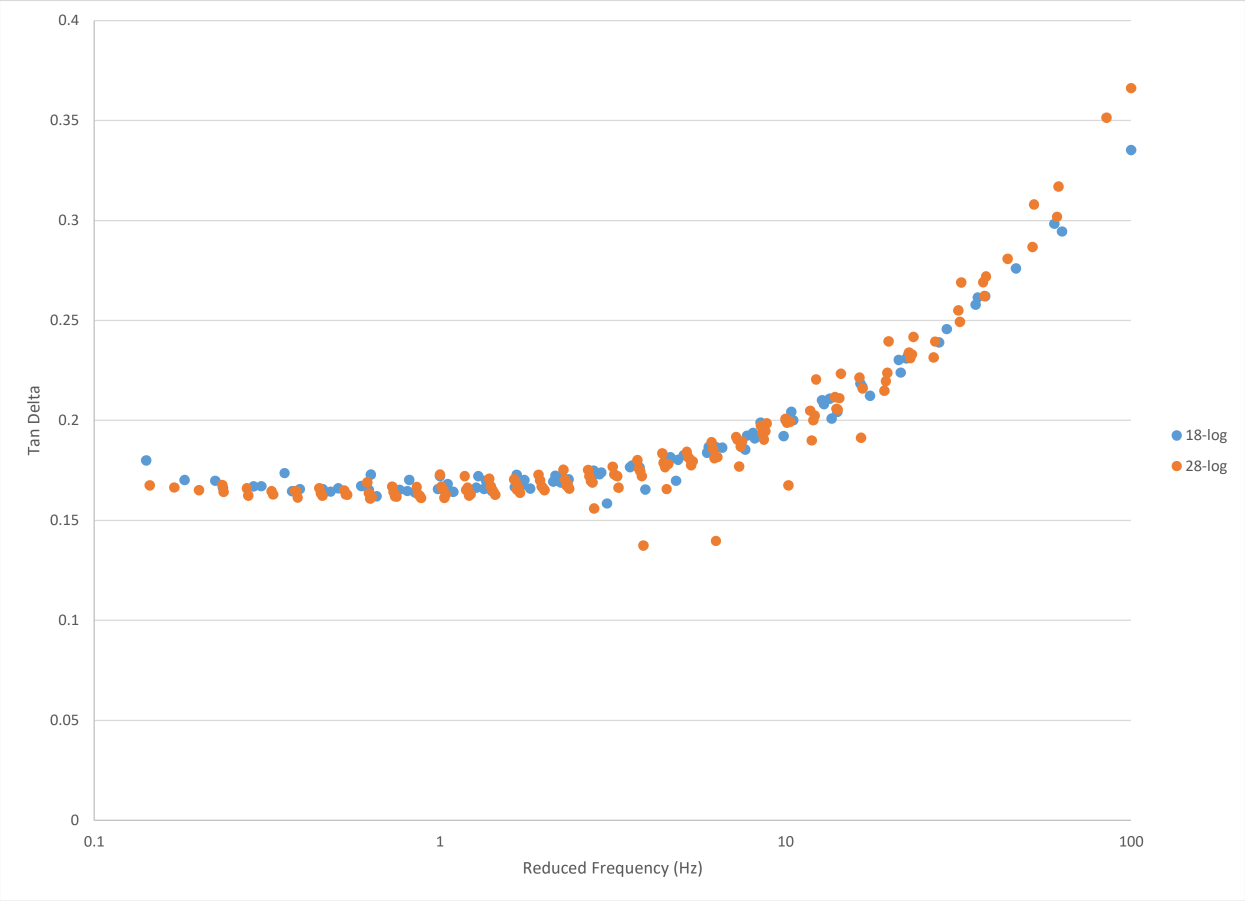

Figure 12: Frequency Evaluation: 28 log steps vs. 18 log steps (orange vs. blue)

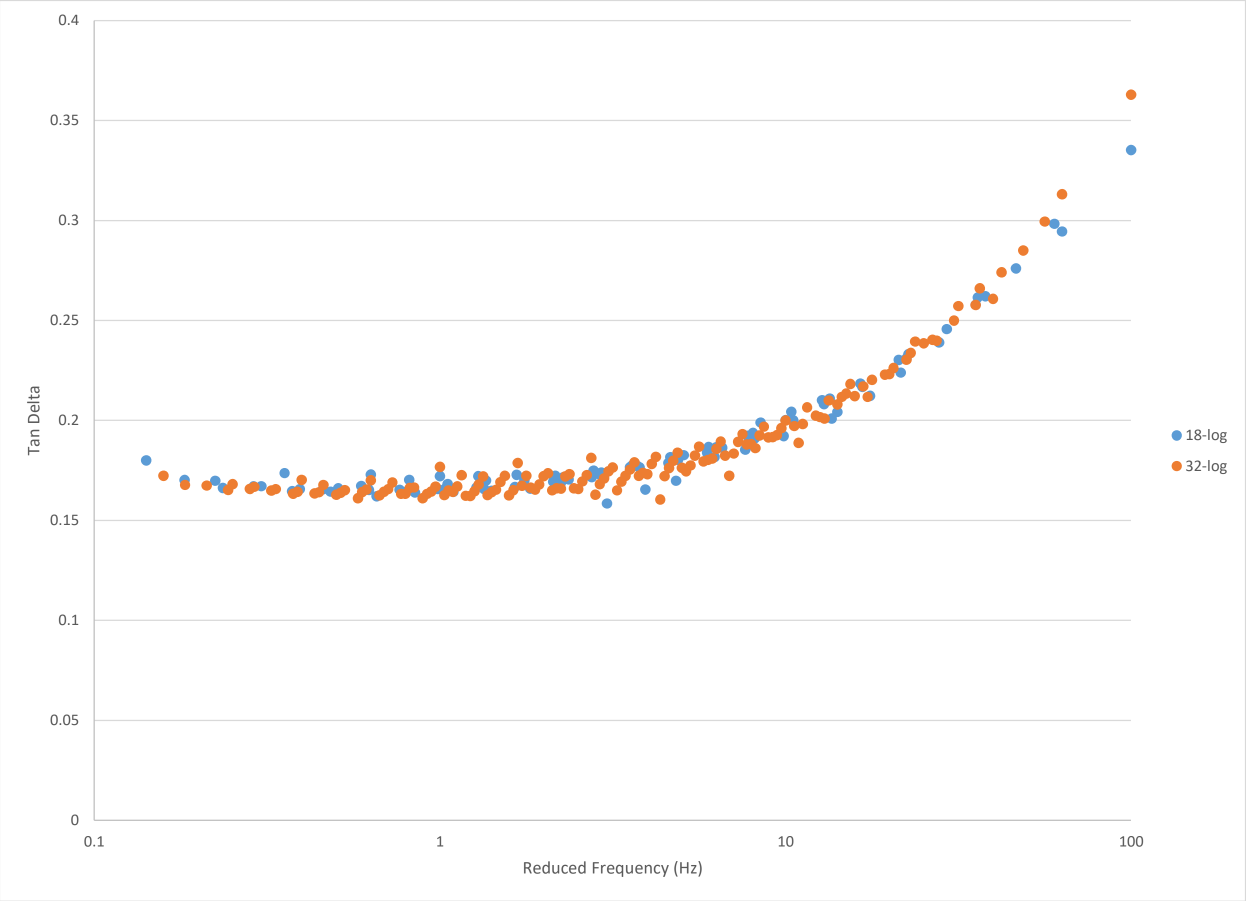

Figure 13: Frequency Evaluation: 32 log steps vs. 18 log steps (orange vs. blue)

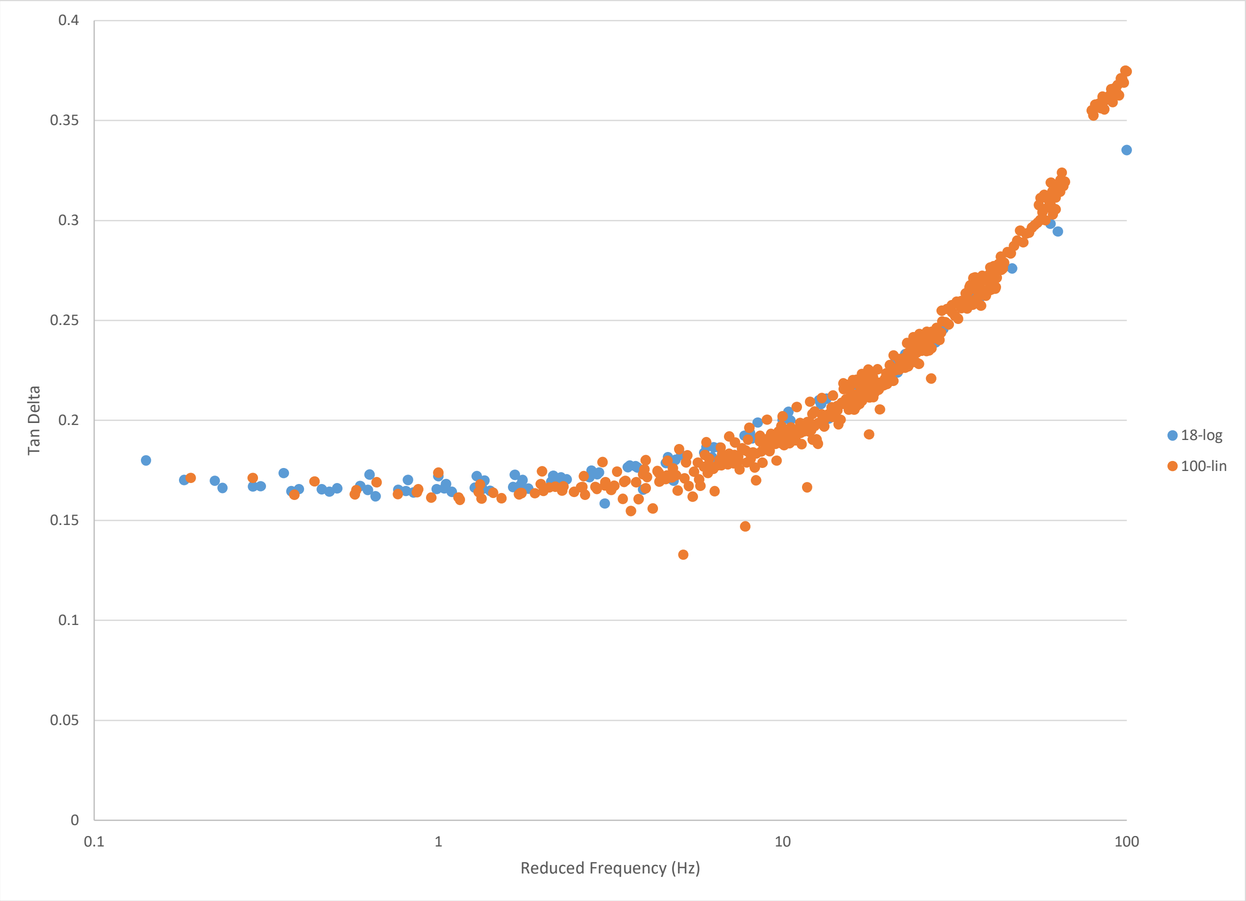

Figure 14: Frequency Evaluation: 100 linear steps vs. 18 log steps (orange vs. blue)

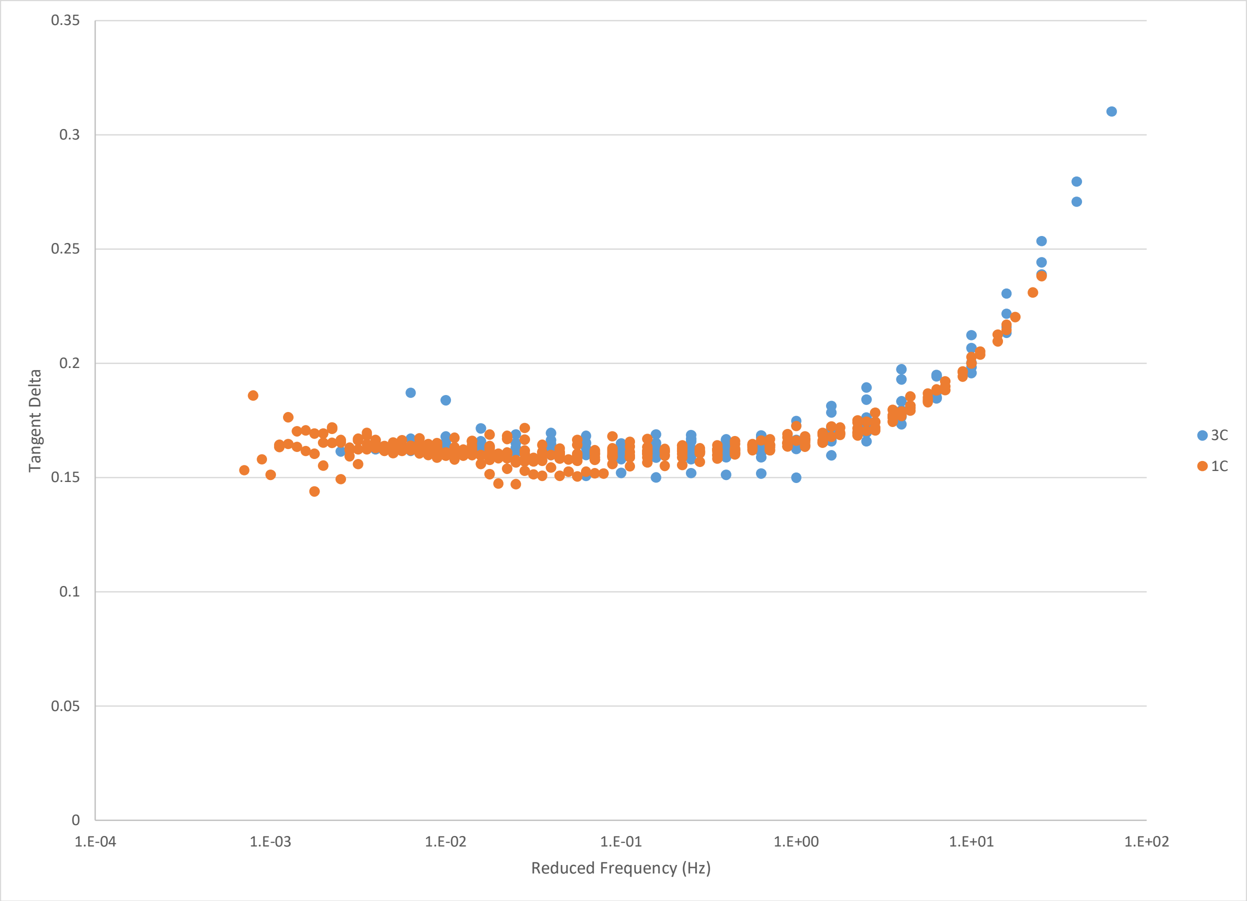

Figure 15: Temperature Evaluation: 1°C steps vs. 3°C steps (orange vs. blue)

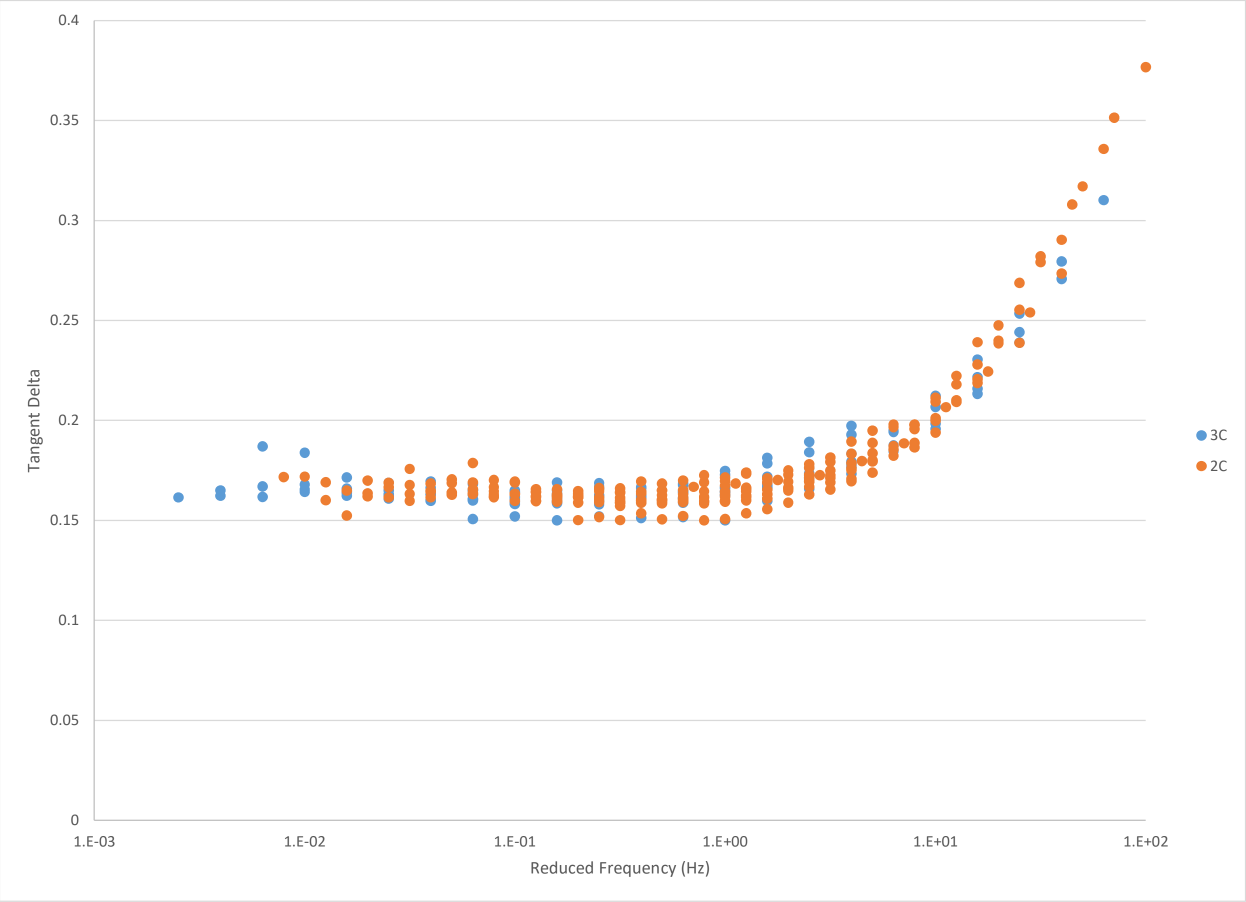

Figure 16: Temperature Evaluation: 2°C steps vs. 3°C steps (orange vs. blue)

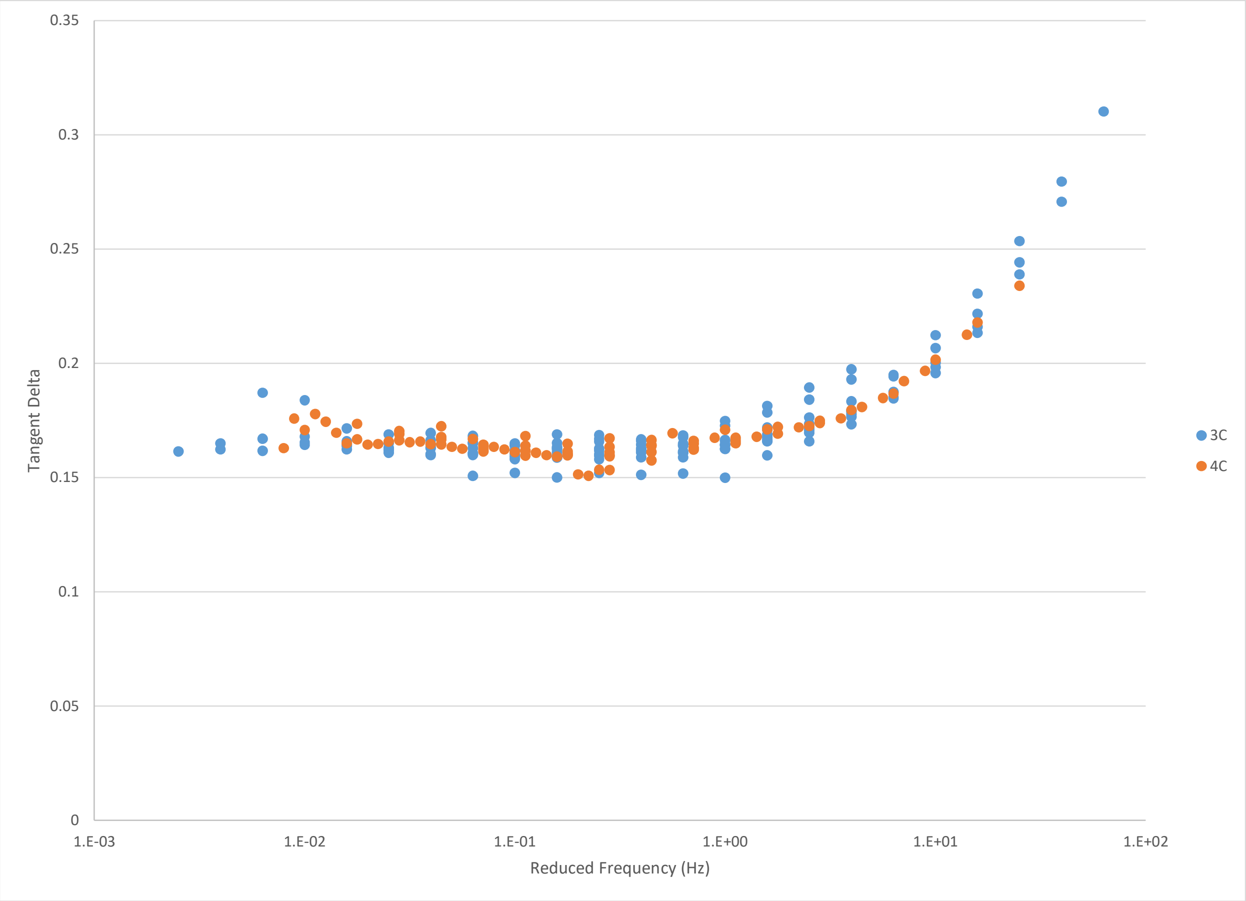

Figure 17: Temperature Evaluation: 4°C steps vs. 3°C steps (orange vs. blue)

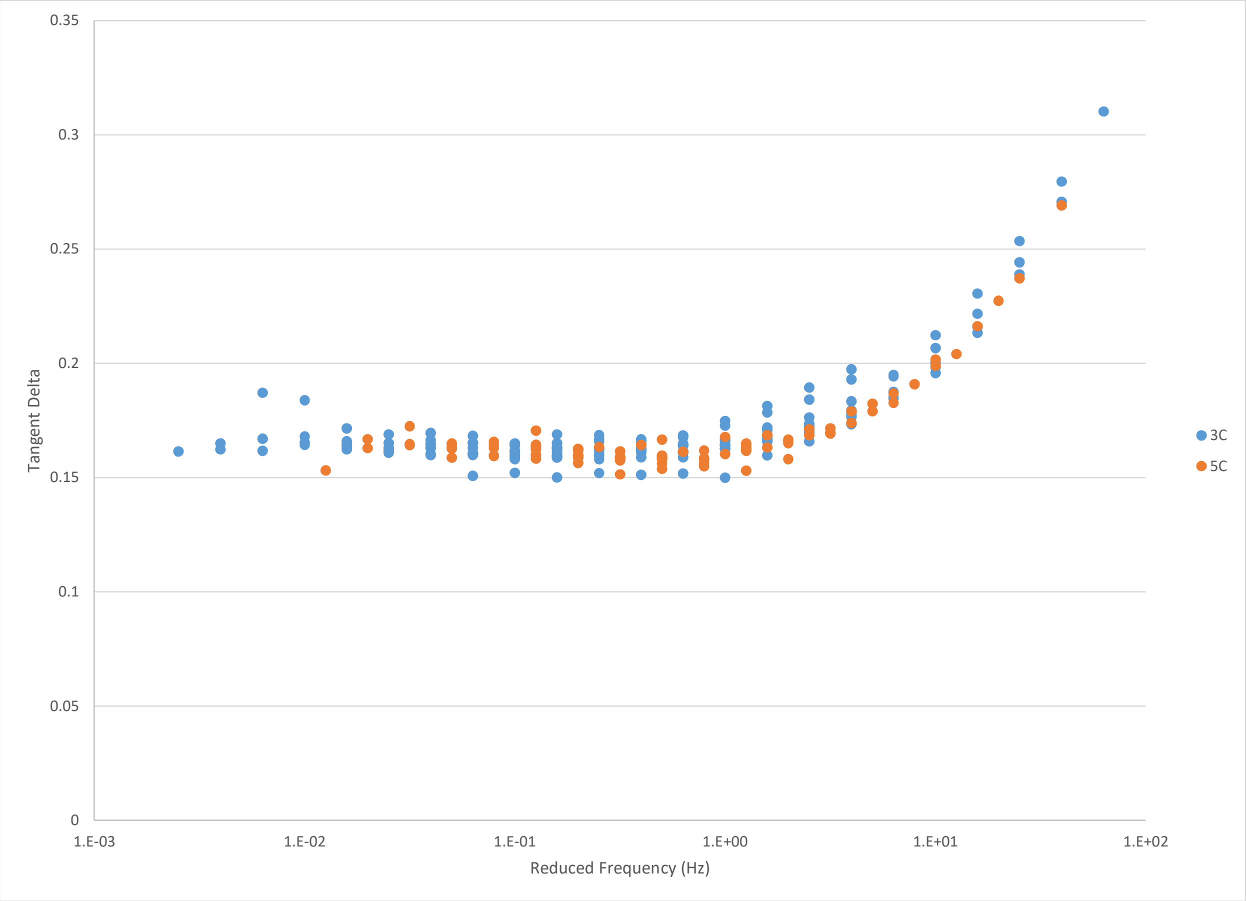

Figure 18: Temperature Evaluation: 5°C steps vs. 3°C steps (orange vs. blue)

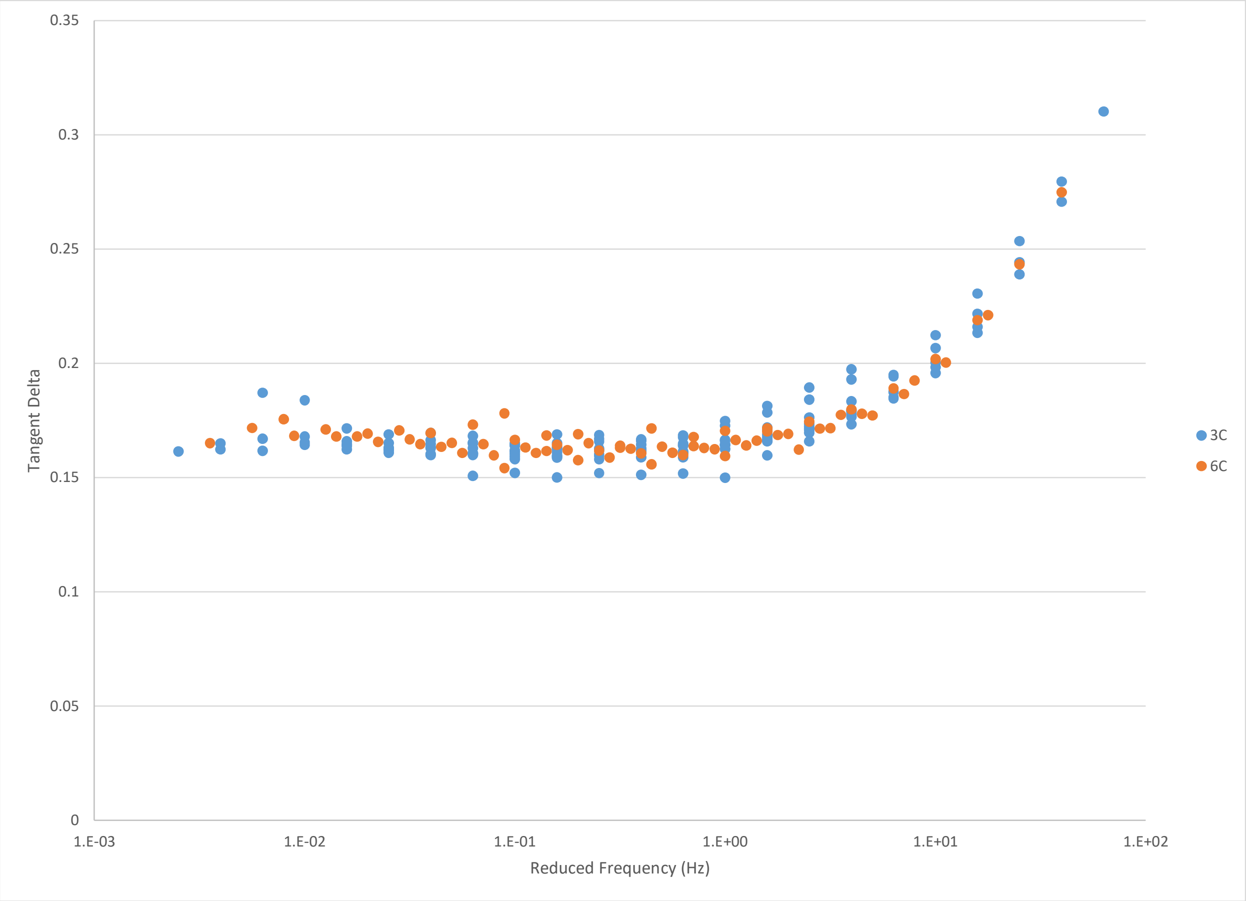

Figure 19: Temperature Evaluation: 6°C steps vs. 3°C steps (orange vs. blue)

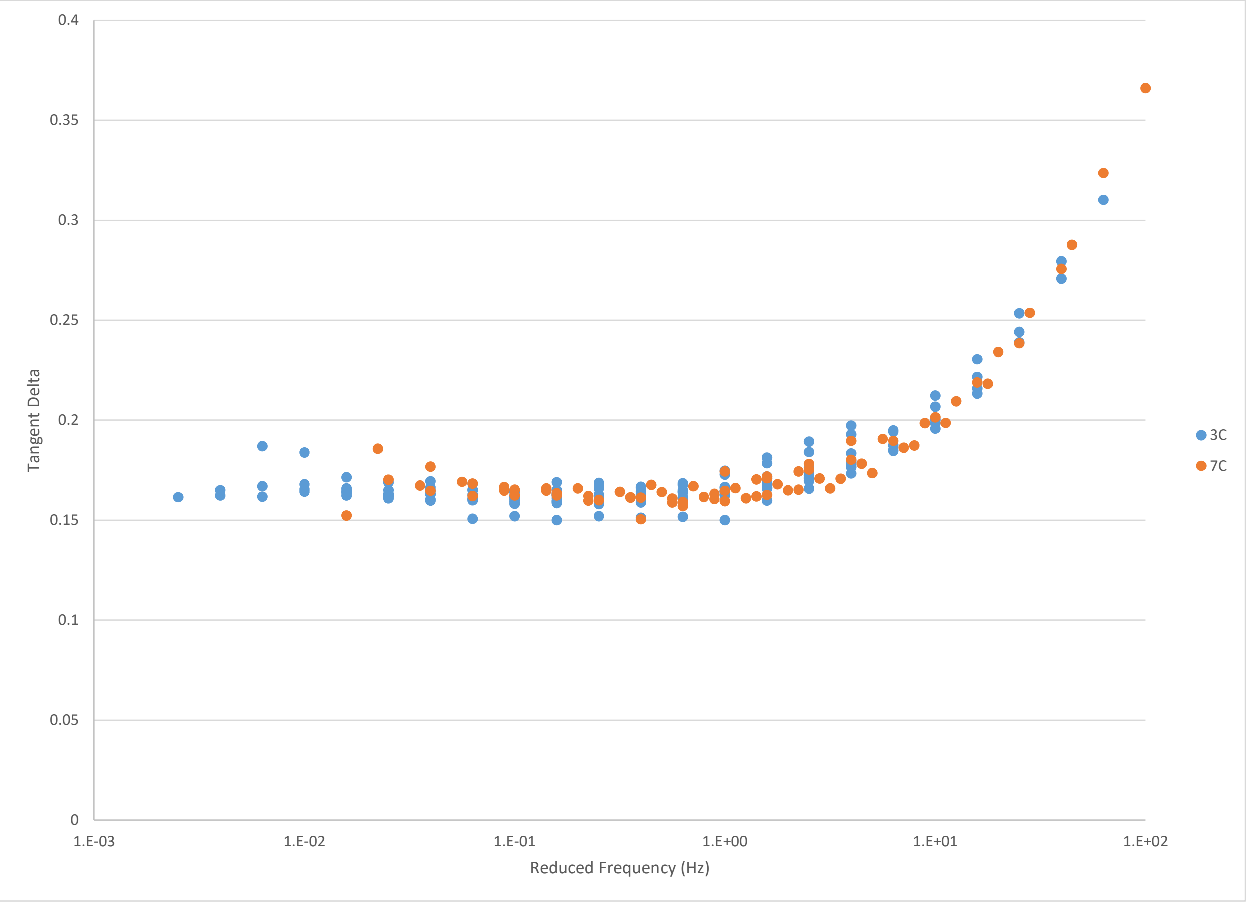

Figure 20: Temperature Evaluation: 7°C steps vs. 3°C steps (orange vs. blue)

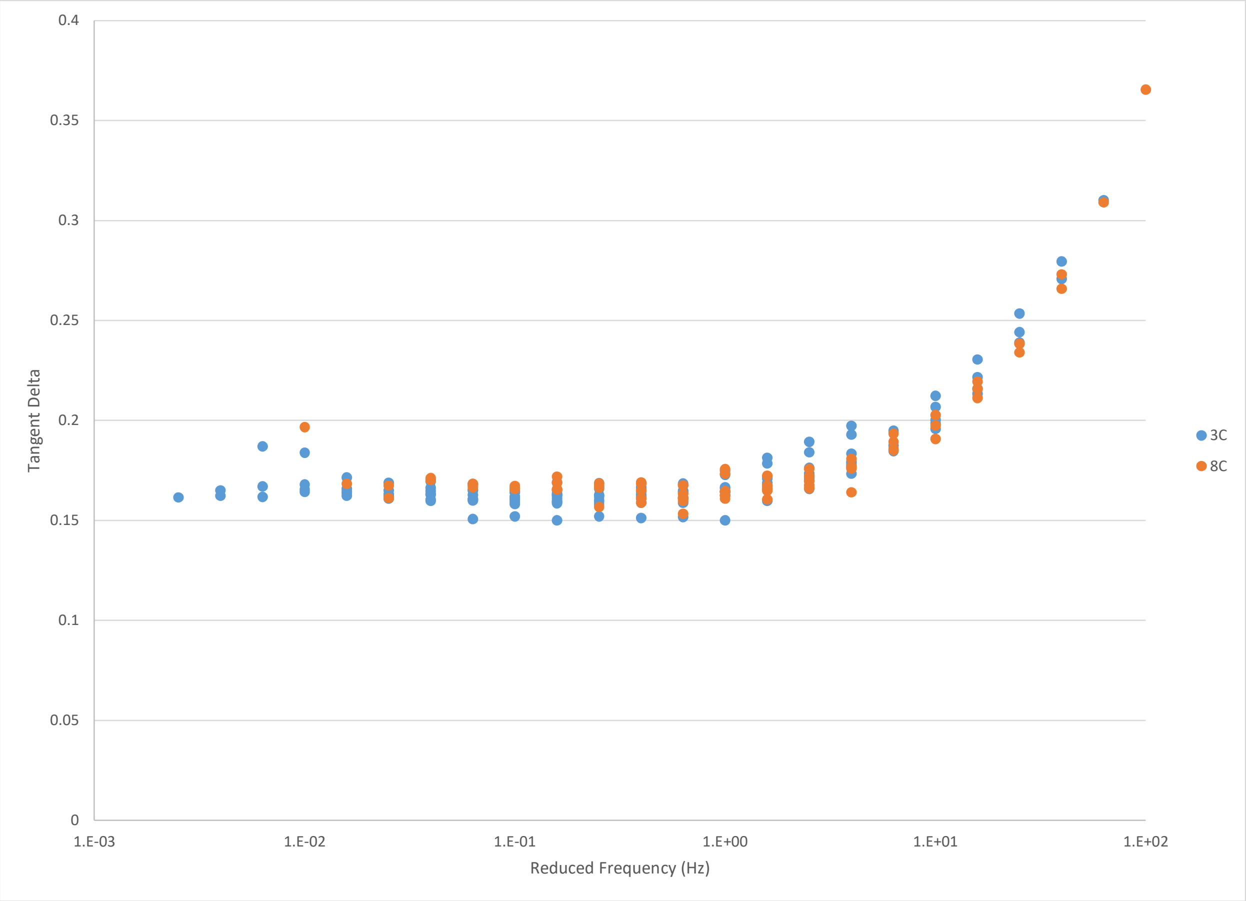

Figure 21: Temperature Evaluation: 8°C steps vs. 3°C steps (orange vs. blue)

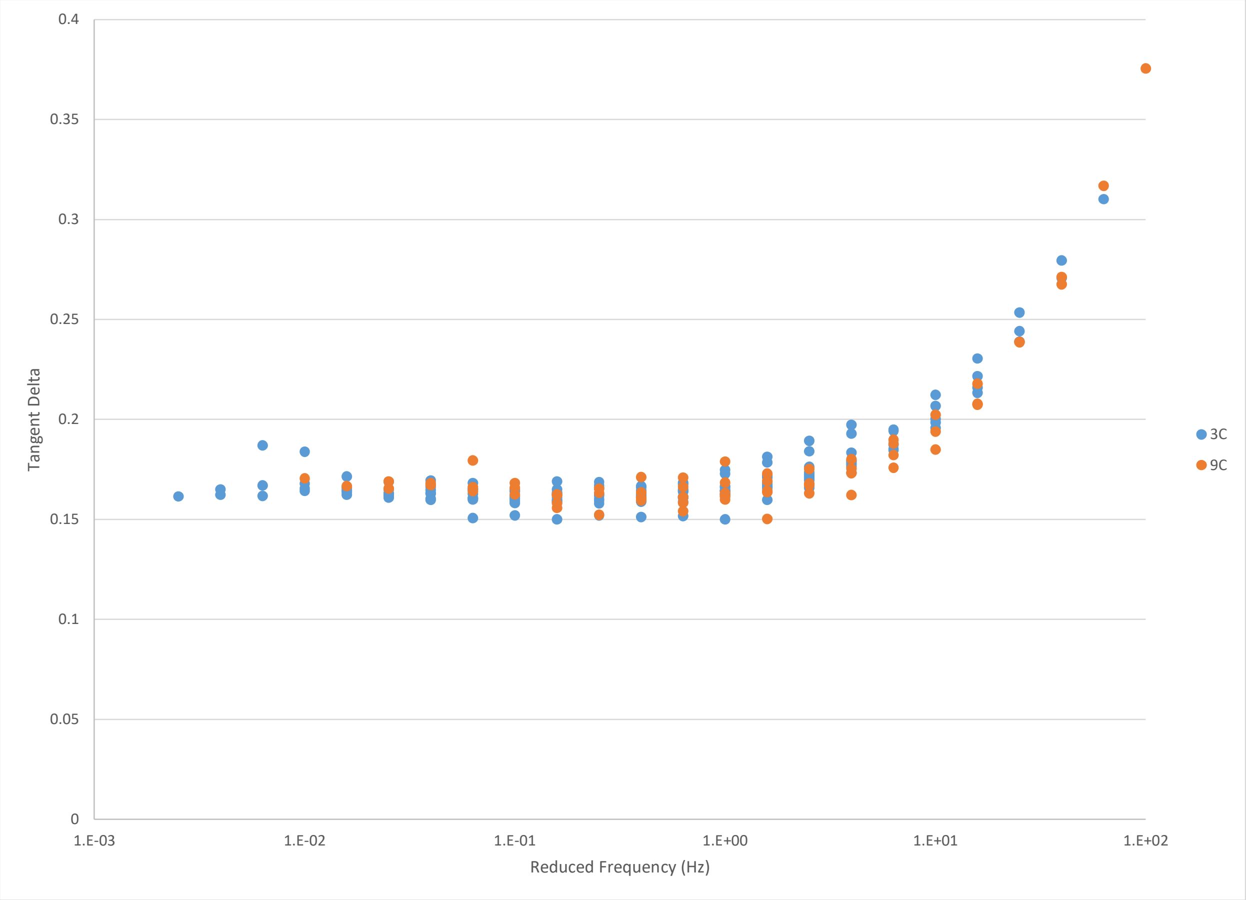

Figure 22: Temperature Evaluation: 9°C steps vs. 3°C steps (orange vs. blue)

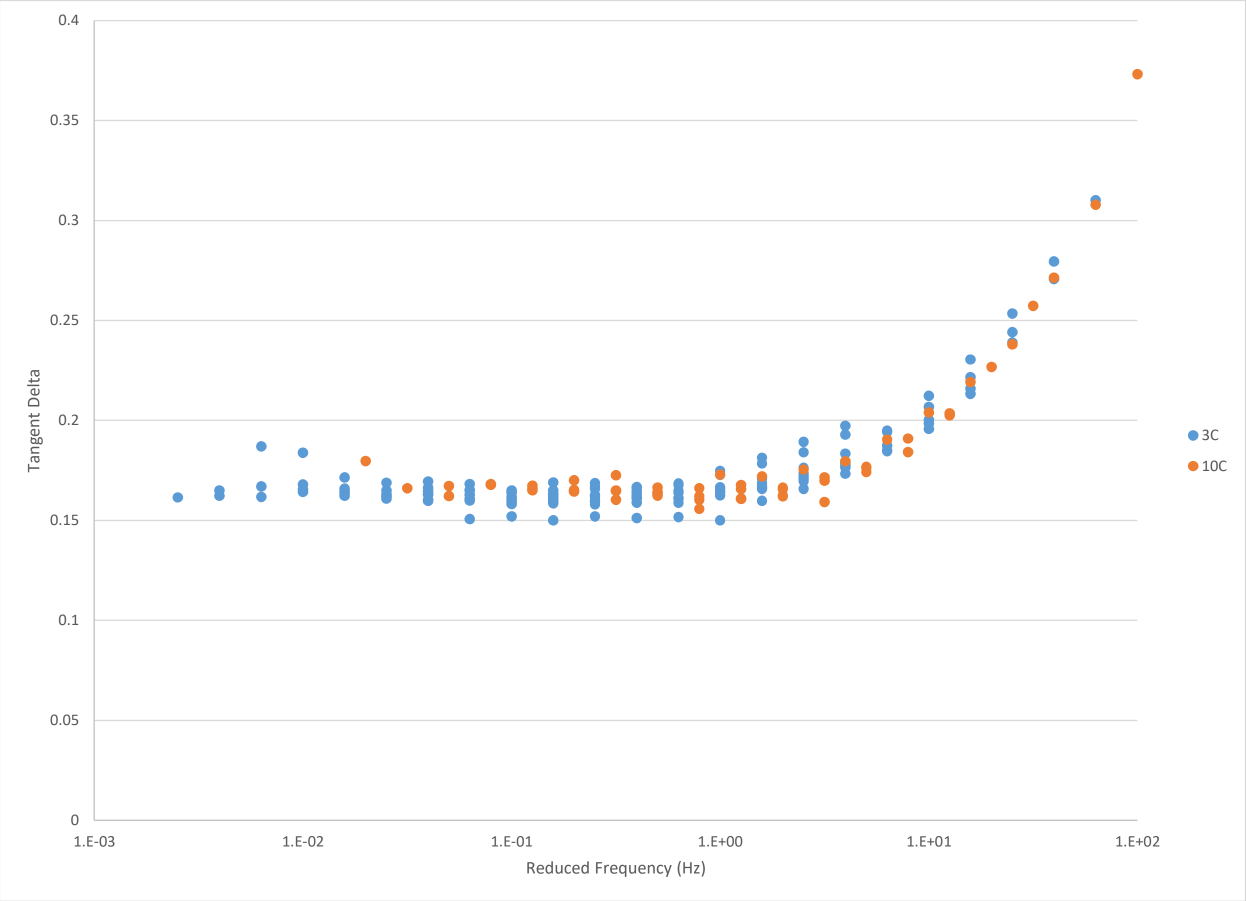

Figure 23: Temperature Evaluation: 10°C steps vs. 3°C steps (orange vs. blue)